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Cadmium, Copper, Lead and Zinc Contents of the Mangrove Oyster, *Crassostrea corteziensis*, of Seven Coastal Lagoons of NW Mexico

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Abstract The ranges of concentrations of Cd, Cu, Pb and Zn of the soft tissues of *C. corteziensis* collected in seven coastal lagoons of NW Mexico were 1.55–7.45, 17.50–166.36, 4.13–9.49 and 245.34–2,304.12 µg/g (dry weight), respectively. Their distributions were not consistent and there were no seasonal trends, indicating different point sources of the metals in each lagoon. The mean Cd and Pb concentrations were 5.34 and 6.30 µg/g (dry weight), which are higher than the values indicative of polluted areas. Our data indicate that only the levels of Cd are a possible health risk in six of these lagoons, and only in the case of regular local consumers. In one, Cu and Zn reach levels of concern.

Keywords Metal pollution · Bivalves · Coastal lagoons · NW Mexico

Aquatic organisms accumulate metals from food, water and sediments, to concentrations that may exceed those of their environment. Their metal contents tend to be higher in estuarine and coastal water bodies, which receive significant inputs from natural sources, as well as from industries and agricultural or metropolitan areas. To assess the quality of these environments, bivalve molluscs (mainly *Mytilus* and *Crassostrea*) have been used worldwide as sentinel species in pollution monitoring programs (Cantillo 1998).

There is evidence that the metal levels are increasing in the coastal lagoons of the Mexican Pacific, and the mangrove oyster *Crassostrea corteziensis* has been suggested as a potential sentinel of the status of these environments, because of its wide distribution, abundance and availability. In addition, knowledge of its metal contents is important, since it is used for human consumption (Páez-Osuna et al. 1991, 1993; Frías-Espericueta et al. 2005).

This study concerns the Cd, Cu, Pb and Zn contents of the soft tissue of specimens of this species collected in seven coastal lagoons of the state of Sinaloa, NW Mexico, which are nursery and feeding areas for many species of commercial interest and support traditional fisheries, as well as important shrimp and oyster culture developments.

Materials and Methods

The samples were obtained every 2 months between March 2006 and January 2007 in the coastal lagoons of Navachiste (NA), Santa María-La Reforma (SML), Altata-Ensenada del Pabellón (AEP), Ceuta (CE), Urías (UR), Huizache-Caimanero (HUC) and Teacapán-Agua Brava (TAB) (Fig. 1). All support traditional fisheries and semi-intensive shrimp culture and, with the exception of Urías, all receive the same type of anthropogenic discharges (rural communities and agricultural effluents). AEP receives also municipal and industrial wastewaters from the cities of Culiacán and Navolato (≈950,000 inhabitants). Urías

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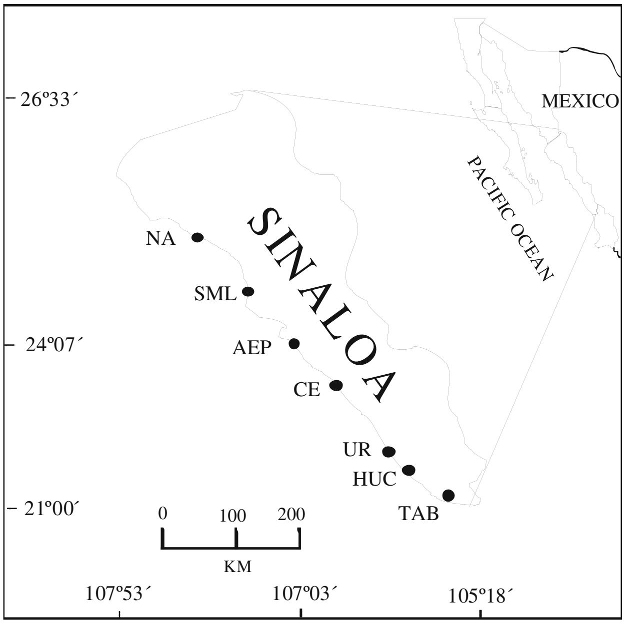

Fig. 1 Location of the seven lagoons

receives mainly the wastewaters of the city of Mazatlán (≈400,000 inhabitants), of its fishing harbour and of the related fish and shrimp-processing industries.

The number of sampling sites depended on the size and morphology of each lagoon, as well as on the presence of red mangrove (*Rhizophora mangle*) stands: because of their large surface area, we obtained three samples in NA and AEP, and two in the mid-sized SML, CE, TAB. In these cases, the station number indicates the progressive distance from the lagoon mouth. UR and HUC had only one sampling site, in the first case because of its small size and in the second because of limited accessibility to the mangrove stands. In all cases, one sample was 100 oysters of commercial size (between 5 and 7 cm shell height).

The organisms of each sample were kept in ice boxes in metal-free separate plastic bags. In the laboratory, they were shucked, the soft tissues were weighed before and after freeze-drying (water content 76%–83%, mean = 79.8%), ground and homogenized in a teflon mortar.

Triplicate 1 g subsamples, spiked with known amounts of the four metals, were digested in 25 ml concentrated HNO_3 (trace metal analysis), evaporated slowly to dryness (90°C) and the solid residue was redissolved in 2 M HNO_3. Finally, the samples were centrifuged and the supernatant was used for metal analysis by flame atomic absorption spectrophotometry (detection limit: 0.01 μg/g).

The purity of reagents and the presence of possible contaminants were determined with one blank for each set of 5–6 samples, using the same procedure used for the samples. All material used for sample handling and for metal analysis was acid-washed, and the accuracy and precision of the method were assessed using reference material MA-M-2/TM (IAEA 1987). The percentages of recovery ranged from 89.5% to 106.5%, and were similar to those calculated from the readings of the spiked samples.

The mean values of the different stations of each lagoon were compared by one-way repeated measures analysis of variance (ANOVA), parametric or nonparametric depending on the normality and equal variances of the data, separating the different means with Tukey's or Dunn's tests. The mean metal concentrations of the samples of the dry and rainy season (November–May and July–October) were compared with Student's *t* or Mann–Whitney's tests. In all cases the level of significance was $\alpha = 0.05$.

Results and Discussion

The distributions of the metal concentrations showed different tendencies in the lagoons with more than one sampling site. NA, TAB and CE tended to have higher values in the stations close to the mouth, but the only significant differences were the higher values of Cd, Cu and Pb in NA, and that of Zn in CE (Table 1).

In SML the distribution of the mean metal contents showed an opposite trend (higher values in the inner station), but the differences were significant only for Cd and Zn. In AEP, Cd was highest in the samples obtained close to the mouth (station 1), whereas the highest values of Cu and Zn were those of station 3, located in the inner lagoon (Table 1).

These differences between stations in the same lagoon show that the distribution of these metals does not depend exclusively on tidal and internal currents, and seems to be mainly related to the location of their local sources.

Comparing the mean values calculated using all samples of each lagoon, there was a similar lack of clear geographic trends. The oysters of Urías had the highest contents of Zn and Cu, the lowest Cd and shared low Pb values with NA, SML and HUC. On the other hand, the highest mean contents of Cd were found in NA (where we found low values of Zn and Pb), as well as in CE. This had low values of Zn and Cu, but the second highest value of Pb (Table 2).

The alluvial plains of northern and central Sinaloa are among the most productive areas of Mexican agriculture and are mainly dedicated to intensive agriculture, which uses large quantities of Cu and Zn-based products for crop protection. For this reason, we expected to find high metal contents in the oysters of the northern and central lagoons, whereas the maximum values of these metals were observed in UR, which mainly receives the discharges of Mazatlán harbour and of its thermoelectric power plant as well as industrial and municipal effluents. This seems to show that these discharges are more important sources of Zn and Cu than the agricultural effluents, possibly because

Table 1 Annual mean metal concentrations (μg/g, dry weight) in the soft tissues of *C. corteziensis* of the coastal lagoons of Sinaloa state

Lagoon	Station	Cd	Cu	Pb	Zn
NA	1	7.45 ± 8.20^{c}	81.01 ± 9.11^{b}	5.79 ± 0.92^{b}	445.54 ± 133.62^{a}
	2	5.60 ± 0.55^{a}	48.92 ± 12.50^{a}	4.13 ± 0.85^{a}	350.44 ± 75.10^{a}
	3	6.36 ± 0.73^{b}	51.48 ± 22.91^{a}	4.65 ± 0.50^{ab}	373.36 ± 127.37^{a}
SML	1	5.38 ± 0.54^{a}	41.85 ± 12.01^{a}	4.98 ± 1.45^{a}	287.26 ± 87.40^{a}
	2	6.24 ± 0.63^{b}	61.69 ± 25.83^{a}	5.68 ± 1.23^{a}	536.52 ± 136.74^{b}
AEP	1	5.84 ± 1.00^{b}	80.54 ± 16.98^{a}	6.55 ± 0.84^{a}	$635.52 \pm 30.02^{a*}$
	2	4.29 ± 0.34^{a}	80.13 ± 15.91^{a}	5.25 ± 1.48^{a}	$712.92 \pm 177.22^{ab*}$
	3	4.91 ± 0.67^{ab}	121.40 ± 22.26^{b}	5.33 ± 1.36^{a}	$968.88 \pm 165.56^{b*}$
CE	1	6.76 ± 2.21^{a}	$72.10 \pm 57.11^{a*}$	8.84 ± 4.17^{a}	600.30 ± 145.46^{b}
	2	7.06 ± 2.84^{a}	$29.66 \pm 19.44^{a*}$	7.35 ± 2.30^{a}	245.74 ± 92.85^{a}
UR	1	1.55 ± 0.31	166.36 ± 38.70	6.51 ± 1.17	$2{,}304.12 \pm 357.07$
HUC	1	5.94 ± 2.80	47.38 ± 26.52	4.23 ± 1.36	758.19 ± 463.60
TAB	1	$5.64 \pm 4.64^{a*}$	$47.08 \pm 27.98^{a*}$	9.49 ± 0.42^{a}	$754.37 \pm 598.65^{a*}$
	2	$1.65 \pm 0.42^{a*}$	$17.50 \pm 5.23^{a*}$	9.44 ± 1.40^{a}	$319.94 \pm 47.13^{a*}$

Different superscript letters indicate significant difference between stations of the same lagoon ($\alpha = 0.05$; $a \leq ab \leq b$ and $a < b < c$)

* Nonparametric test

Table 2 Mean Cd, Cu, Pb and Zn contents (±SD) of *C. corteziensis* of seven lagoons of NW Mexico

Lagoon	Cd*	Cu*	Pb*	Zn*
NA	6.47 ± 1.02^{c}	60.46 ± 21.11^{ab}	4.86 ± 1.02^{a}	389.58 ± 114.66^{a}
SML	5.81 ± 0.71^{bc}	53.77 ± 22.77^{a}	5.32 ± 1.32^{a}	411.89 ± 170.19^{a}
AEP	5.01 ± 0.94^{bc}	94.02 ± 26.42^{b}	5.71 ± 1.32^{a}	72.44 ± 196.99^{bc}
CE	6.91 ± 2.41^{c}	50.88 ± 46.02^{a}	8.09 ± 3.27^{ab}	423.02 ± 219.44^{a}
UR	1.55 ± 0.31^{a}	166.36 ± 38.70^{b}	6.51 ± 1.17^{ab}	$2{,}304.12 \pm 357.07^{c}$
HUC	5.94 ± 2.80^{bc}	47.38 ± 26.52^{ab}	4.23 ± 1.36^{a}	58.19 ± 463.60^{ab}
TAB	3.64 ± 3.75^{ab}	32.29 ± 24.53^{a}	9.46 ± 0.97^{b}	37.18 ± 461.18^{ab}

Different superscript letters indicate significant differences between lagoons (Kruskall–Wallis and Dunn's tests in all cases, $\alpha = 0.05$. $a \leq ab \leq b$ and $a < b$)

* Nonparametric test

of the Cu-based antifouling paints used in the shipping industry, and of the wastewaters of the fish processing industry, since marine fish are good sources of both metals (Çelik and Oehlenschläger 2004) and especially of Zn (Gibson and Hotz 2001).

Seasonal variations of the metal contents of aquatic organisms have been described in other agricultural regions (Kargin 1996), but the only significant difference found in this study was the higher Pb value found in CE in the dry season (6.07 ± 2.22 and 11.10 ± 1.83 μg/g of dry tissue in the dry and rainy season, respectively), possibly because the volumes of continuous anthropogenic discharges received by these lagoons exceed the variations of continental inputs caused by the alternance of dry and wet season (De la Lanza-Espino and Flores-Verdugo 1998).

According to our data, these lagoons do not seem yet highly impacted by anthropogenic activities, since the mean metal contents of their mangrove oysters are lower than the 85th percentile values reported for mussels and oysters by the Worldwide Mussel Watch (12, 16, 680, and 4,500 μg/g, respectively: Cantillo 1998). In addition, most of our data do not show a clear trend to increasing metal levels in the coastal lagoons of NW Mexico, since they are within the ranges found in previous studies. The notable exceptions are the progressively higher Cu and Zn contents of the oysters of Urías, which seem to indicate a progressive deterioration of this system (Table 3).

Most of the Pb and Cd concentrations were higher than the values indicative of polluted areas (Cd > 3.7 μg/g and Cu > 3.2 μg/g: Cantillo 1998). In the first case, this could be due to Pb released from the sediments, where it probably accumulated in previous years, when Pb was used as antiknock agent in Mexican gasoline, although the natural background values of the alluvial soils of the Pacific coastal plains are possibly more important sources of this, as well as other metals (Páez-Osuna 1999).

Table 3 Ranges or mean values of the concentrations of Cd, Cu, Pb and Zn in the soft tissues of *C. corteziensis* of some lagoons of the Mexican Pacific

Source	Cd	Cu	Pb	Zn
Urías				
Páez-Osuna and Marmolejo-Rivas (1990)	0.8–1.8	25–83	1.5–15	710–1,600
Frías-Espericueta et al. (2005)	2.63	76.5	11.6	1,884
This study	1.27–2.08	122.3–200.39	4.95–8.09	1,936.8–2,784.9
Navachiste				
Páez-Osuna et al. (1991)	10.3	67	–	509
This study	4.97–8.55	20.83–95.87	3.11–6.67	184.1–638.4
Altata-Ensenada del Pabellón				
Páez-Osuna et al. (1993)	2–15	147	–	727
Frías-Espericueta et al. (2008)	6.47	71.45	8.36	928.8
This study	3.95–6.44	61.23–144.40	3.31–7.23	517.6–1,242.0
Sinaloa state (ranges and mean values)				
Páez-Osuna et al. (2002)	–	15.4–216	3.6–7.6	442–1,595
		89	5.7	944.3
This study	1.55–7.45	17.50–166.36	4.13–9.49	245.34–2,304.12
	5.34	67.7	6.30	663.7

In the case of Cd, the high mean values (4.29–7.61 µg/g) found in 14 of the 16 stations of these lagoons would be consistent with the fertilizer-enriched agricultural effluents flowing into these systems, since Cd is associated with phosphate fertilizers (Loganathan et al. 2008). UR and TAB would be the exception, because of the almost complete lack of agricultural effluents in the first case, and of the less intensive agricultural practices of southern Sinaloa in the second.

Together with Hg, Cd and Pb are the metals of major concern for human health. To determine the risk level for human consumption of this bivalve, the reference values mentioned in FDA (1993) and WHO (1998) were compared to the mean yearly values of each metal obtained in each lagoon and, since the oysters are sold to wholesalers for their distribution to regional or to national markets, to those calculated using all the samples collected in all lagoons.

According to our results, Cd is the metal of most concern in six out of the seven lagoons, since the regular ingestion of between 40 and 75 g (51.49 g considering the overall mean value) of soft tissue of this oyster would be sufficient to reach the daily suggested limit of 55 µg/person/day (Table 4). Again, the notable exception is the Urías system, where Cd values are of less concern than the levels of Cu and Zn, which would limit the daily consumption to between 90 and 98 g.

Table 4 Amounts of soft tissues of *C. corteziensis* of Sinaloa lagoons equivalent to the levels of concern (in µg of metal/person/day: FDA 1993; WHO 1998) for the daily intake of Cd, Cu, Pb and Zn

Lagoon	Daily ingestion (grams/person)			
	Cd	Cu	Pb	Zn
NA	42.5	248.1	771.6	577.5
SML	47.3	279.0	704.9	546.3
AEP	54.9	159.5	656.7	291.3
CE	39.8	294.8	463.5	531.9
UR	177.4	90.2	576.0	97.7
HUC	46.3	316.6	886.5	296.8
TAB	75.5	464.5	396.4	418.9
Mean	51.5	221.6	595.2	339
Levels of concern (µg)	55	3,000	750	45,000

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